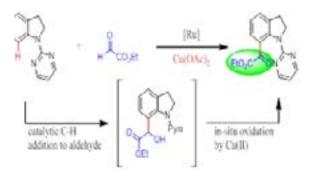
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Synthesis of α -ketocarboxylate group-containing indolines via Ru(III)-catalyzed C-H addition and oxidation

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The C7-functionalized indolines have been recognized as important structural motifs found in a number of natural and L synthetic products. With the development of catalytic functionalizations of inactive C-H bonds, it has become the most attractive strategy leading to C7-functionalized indolines. In this context, acylation, arylation, olefination, alkylation, amination, alkynylation and thiolation of indolines at the C-7 position were described bifunctional. a-ketoesters can act as important backbones in some natural products, such as the 3-deoxy-2-ulosonic acids and their derivatives. In addition, aryl α-ketoesters have been used as useful intermediates for the synthesis of bioactive molecules such as potent inhibitors of proteolytic enzymes, inhibitors of leukotriene A4 hydrolase, photopolymerization initiators, and antisunburn agents. Since a-ketoesters bear two vicinal functional groups, strongly electron-deficient carbonyls and neighboring binding-capable esters, it makes them useful synthons for asymmetric reduction, aminohydroxylation, fluorination, aldol reactions, lactonization, tandem heterocyclization and construction of various bioactive natural products. Due to the significance of α -ketoesters, various classical procedures have been reported including oxidation of a-hydroxyl esters using various kind of oxidants, Friedel-Crafts acylation, oxidation of methyl 2-phenylacetate, hydrolysis and esterification of acyl cyanides, and other methods. In addition, there have been numerous reports for the synthesis of α -ketoesters under metal catalysis or under metal-free conditions with different coupling partners. Recently, the directing group-assisted catalytic addition reaction of inactive C(sp²)-H bonds to carbonyl compounds has emerged as a green and atom economical strategy to afford the corresponding secondary or tertiary alcohols. Very recently, our research group disclosed the catalytic addition reaction of heterocyclic C-H bonds to activated aldehydes or ketones furnishing the corresponding secondary and tertiary alcohols. During the optimization of reaction conditions in the coupling of indolines and ethyl glyoxalate, we found that a Cu(OAc)2 additive provided C7-indolinyl ketoesters as major products instead of alcohol compounds. Inspired by this interesting finding, we herein report the first Ru(II)-catalyzed site-selective acylation of indolinic C-H bonds with ethyl glyoxalate affording C7-indolinyl α -ketoesters.



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